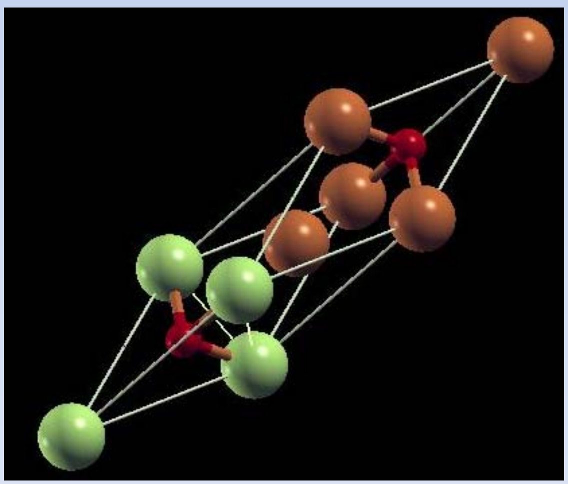
APS physics MARCH MEETING 2014
MARCH 3-7 DENVER
COLORADO CONVENTION CENTER

A DFT Study of Tetragonal Rocksalt Proxy Copper Monochalcogenide Structures:
-- Implications for Possible High-Tc Superconductivity --



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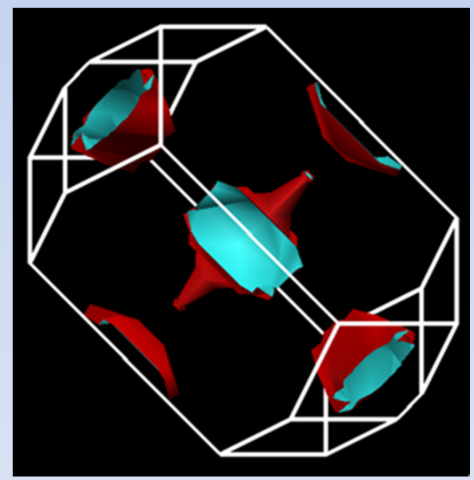


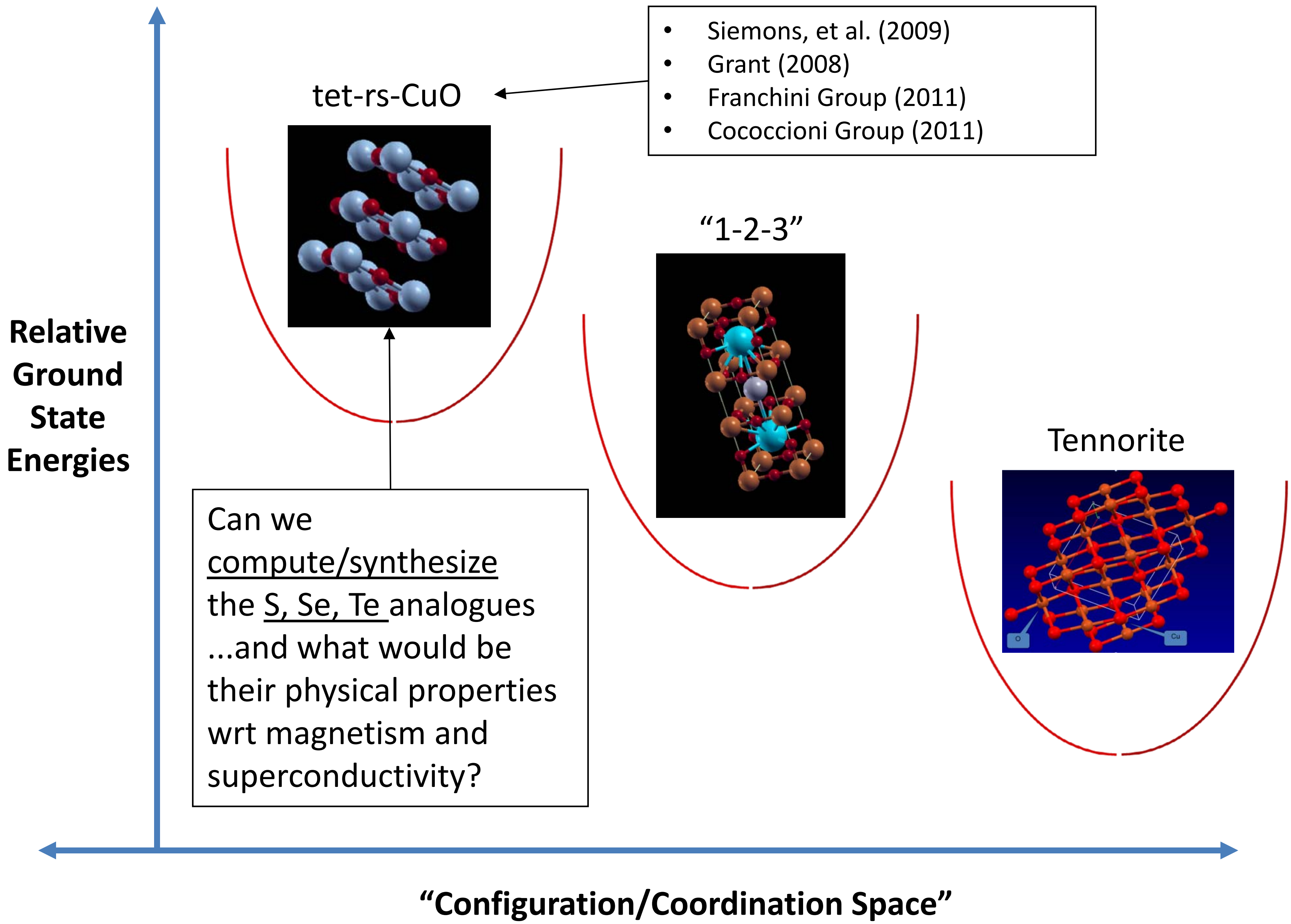
Session Y47
Theory of Strongly Correlated Superconductivity
8 AM – 11 AM, Friday, 7 March

Paper 8
9:24 AM – 9:36 AM
Mile High Ballroom 4F

– Our Computational Tool Box –

- DFT + Hubbard U
  - Quantum Espresso
    - Bands, Fermiologies, States (DOS), Phonons
- Graphics
  - Xcrysden, XMGRACE
    - Bandwidths, Fermi Surfaces, Projected DOS
- Modeling
  - Neel Temperatures a la Van Vleck/Anderson/Hubbard
  - Superconductivity via Eliashberg/McMillan

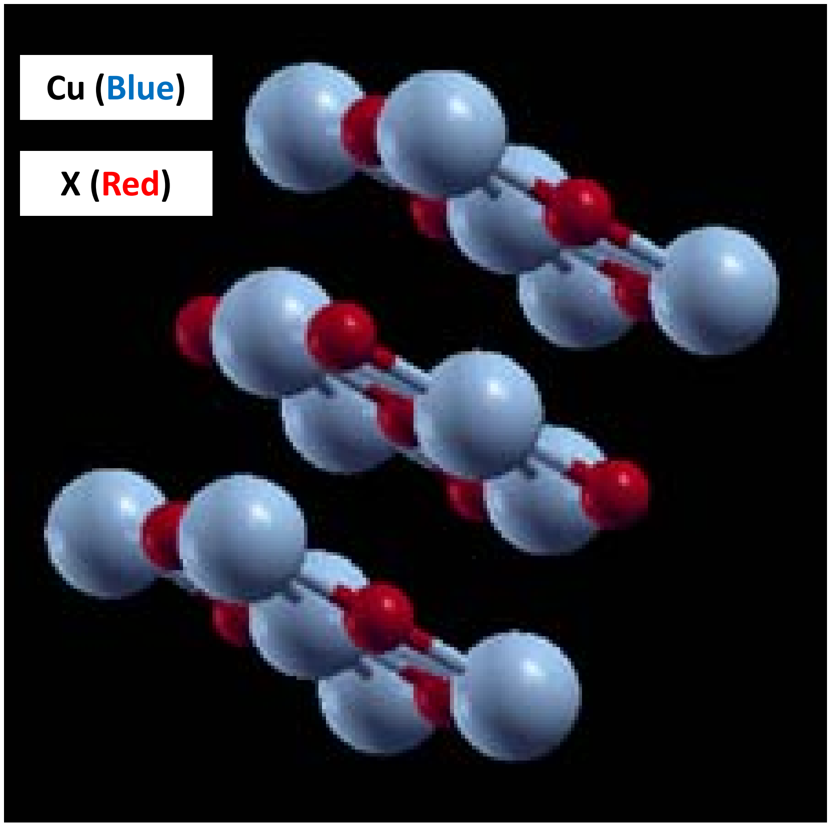
The Various Flavors of Copper "Monoxide"

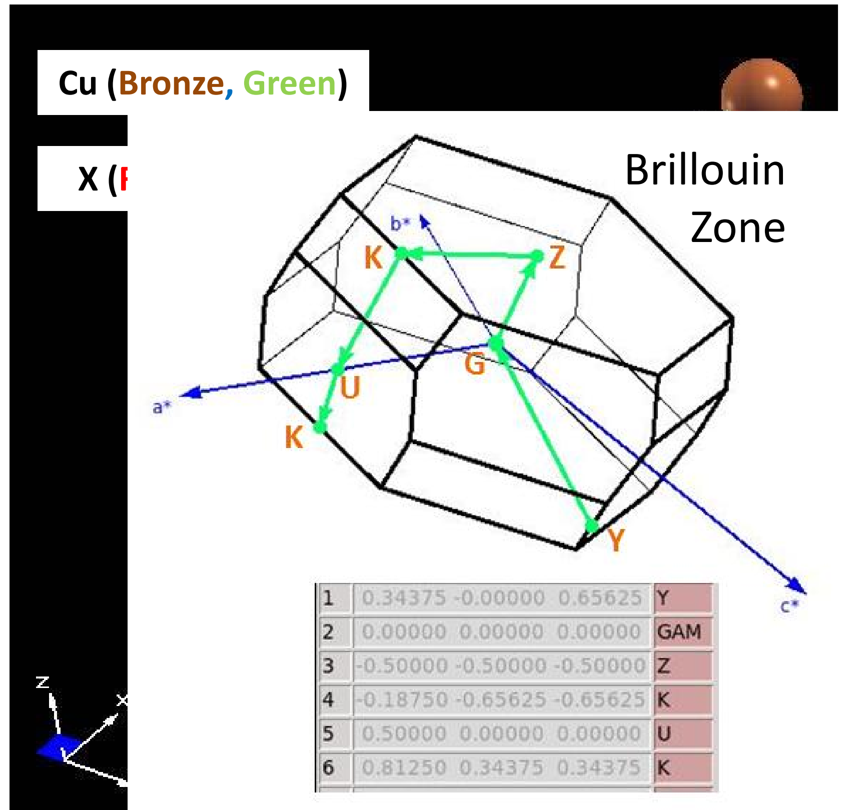


Rocksalt af-CuX Crystallography

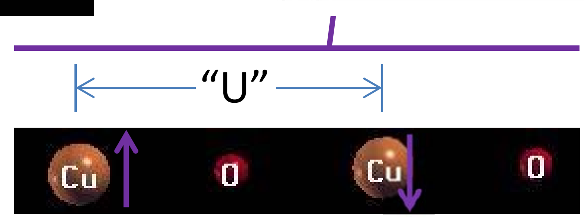
nm-Translational Unit Cell

af-Primitive Cell





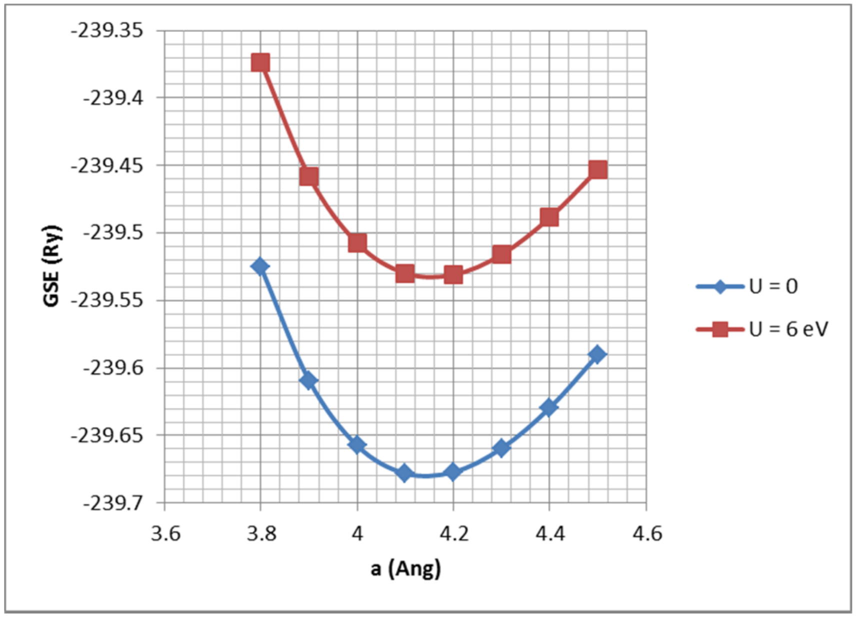
Note: The af-"translationally asymmetric unit"



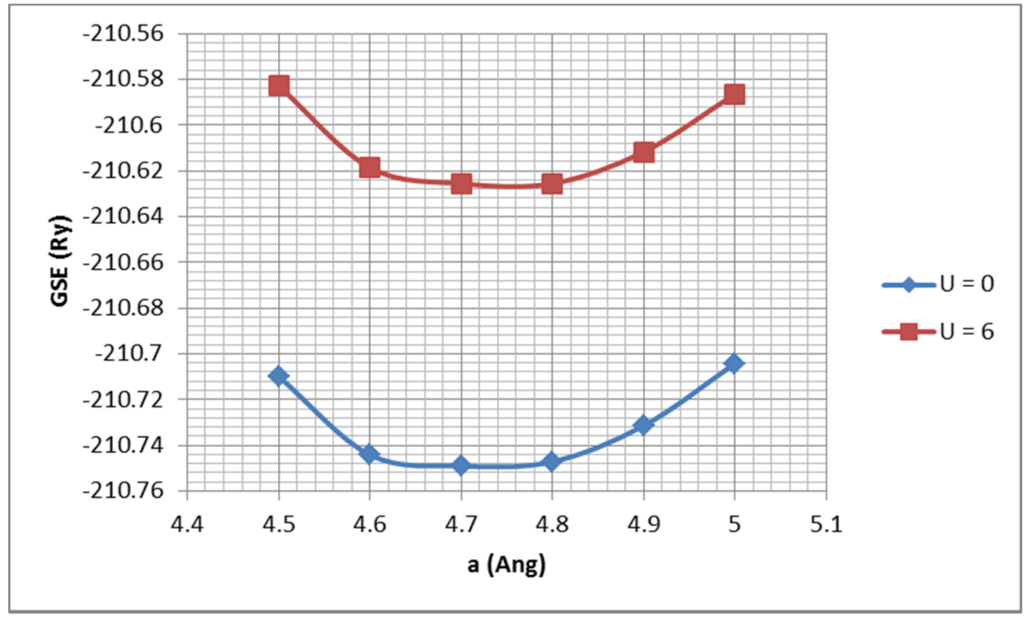
contains two Cu ions to correctly represent the doubly-periodic spin up/down ordering

CuX (Cubic, Equilibrium Lattice Constant(s))

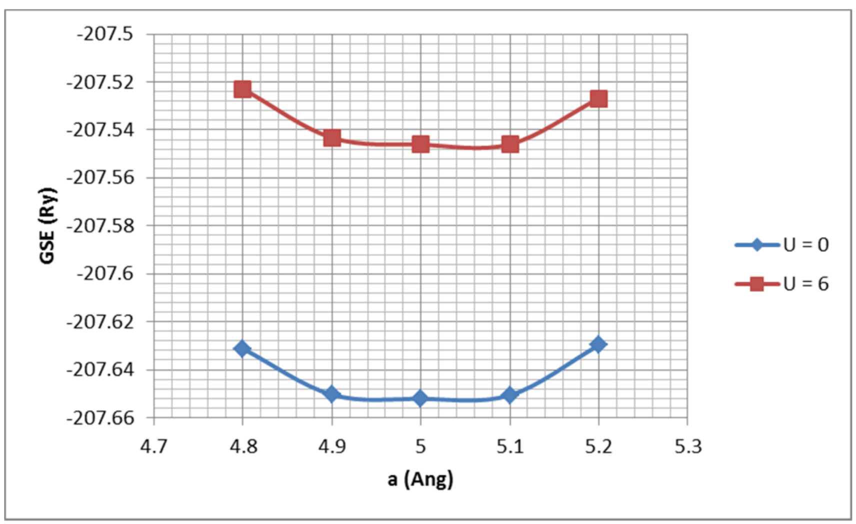
CuO (a ≈ 4.1 Å)



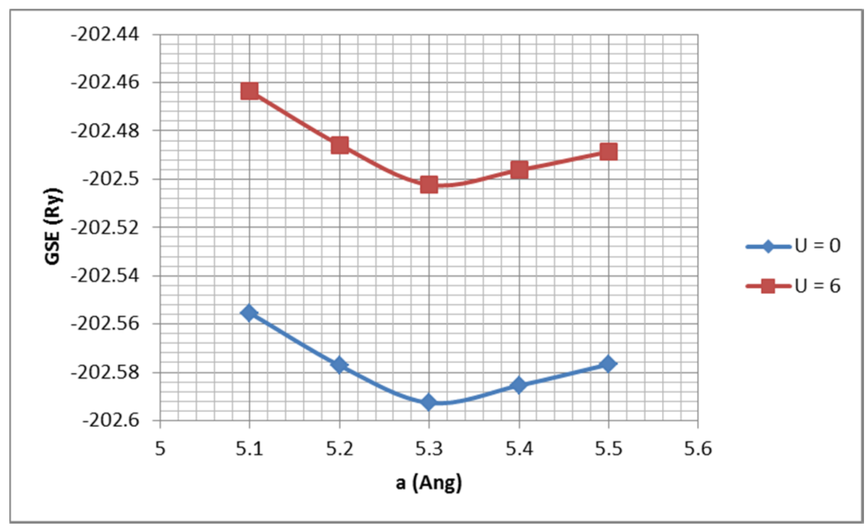
CuS (a ≈ 4.7 Å)



CuSe (a ≈ 5.0 Å)

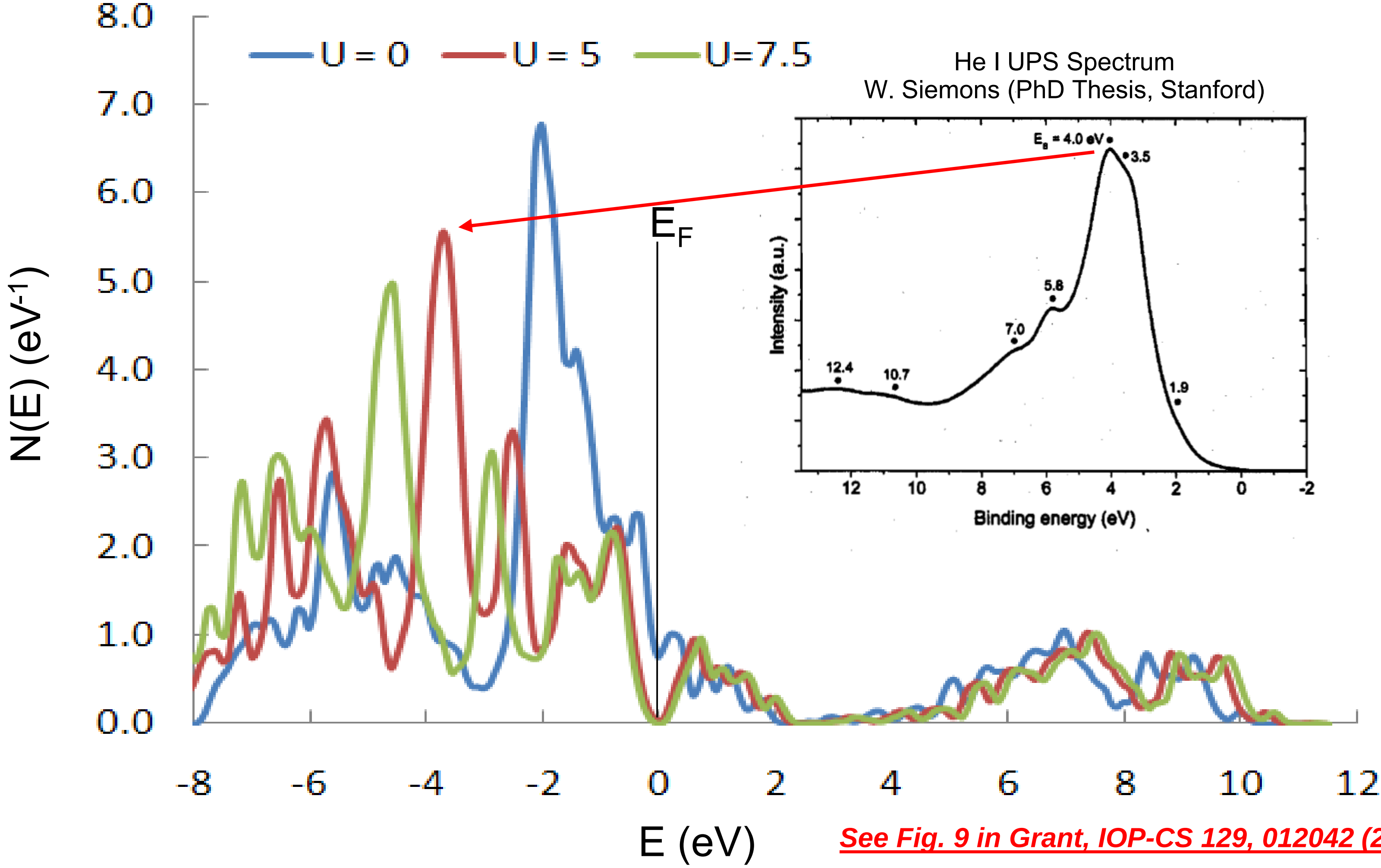


CuTe (a ≈ 5.3 Å)



What Does Experiment Say About Rocksalt CuO?

It's *Tetragonal(!)* for 4-6 monolayers forced-epi grown on STO yielding a film with lattice constants a = b = 3.905 Å, and c/a ≈ 1.3, representing a *5% basal-plane contraction* down from pure cubic having a = b = c = 4.1 Å. (Siemons, et al, PRB 79, 195122 (2009))

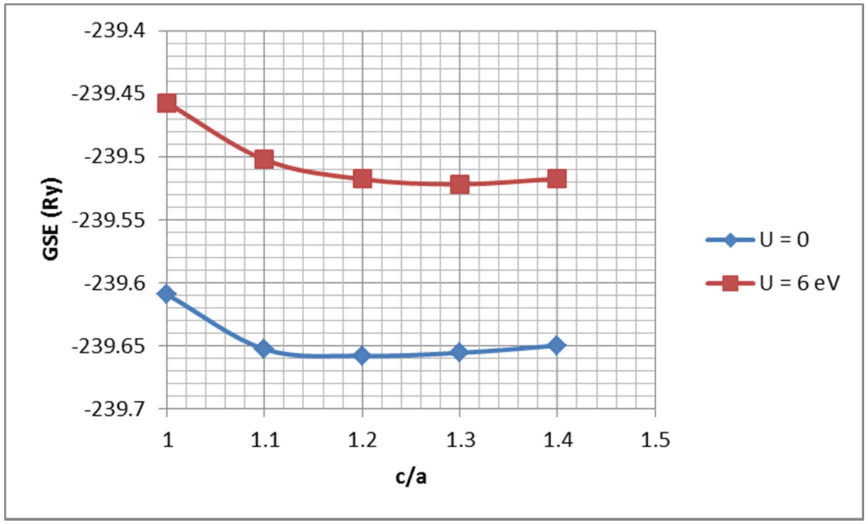


See Fig. 9 in Grant, IOP-CS 129, 012042 (2008)

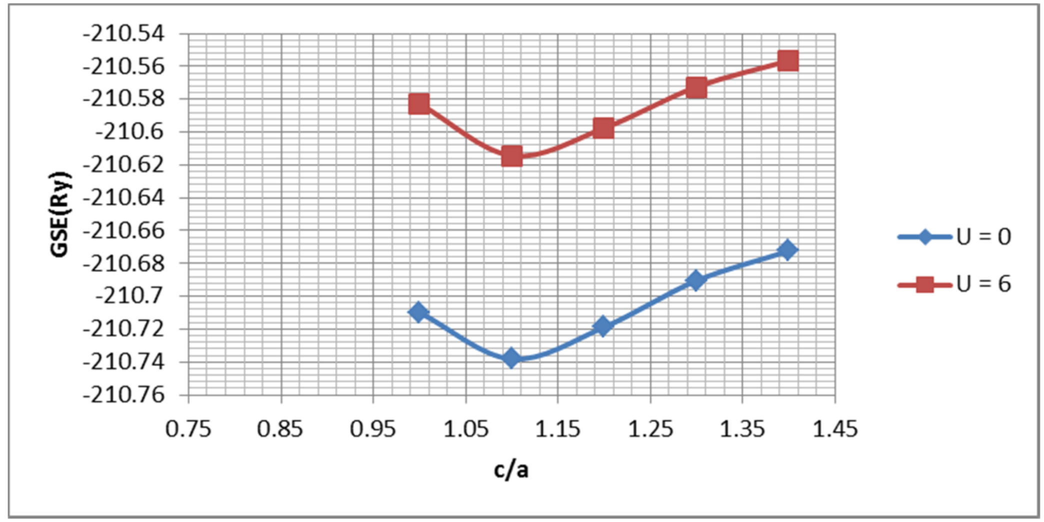
CuX (Tetragonal)

(Assuming a *5% contraction* of the a, b lattice constants *a la CuO on STO*)

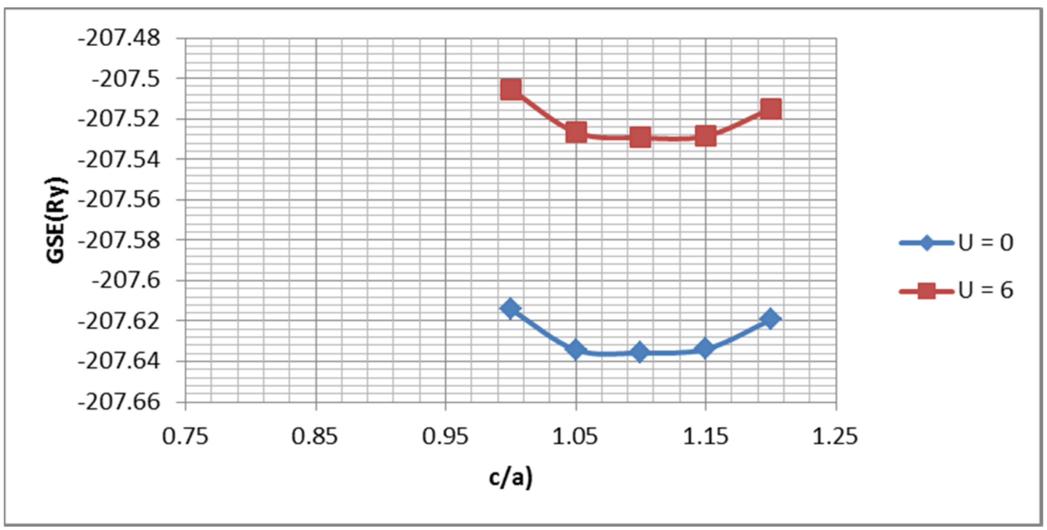
CuO (a = b ≈ 3.9 Å; c/a ≈ 1.3)



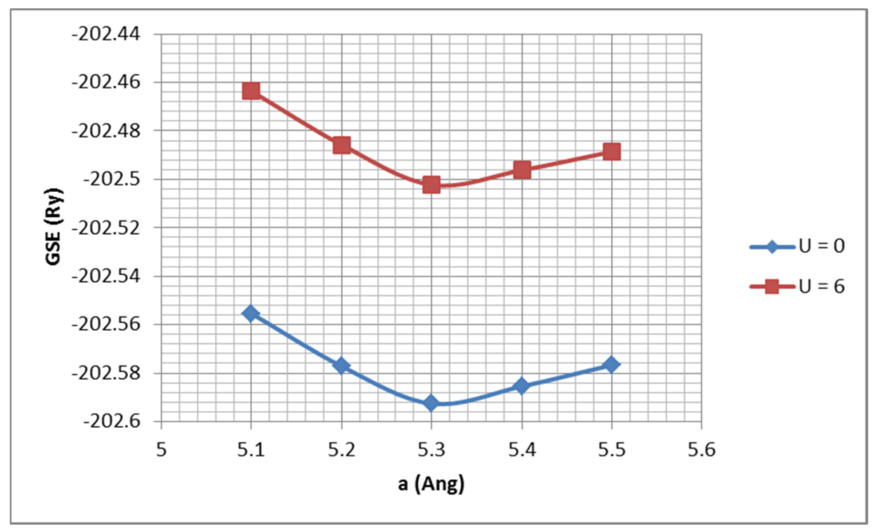
CuS (a = b ≈ 4.5 Å; c/a ≈ 1.1)

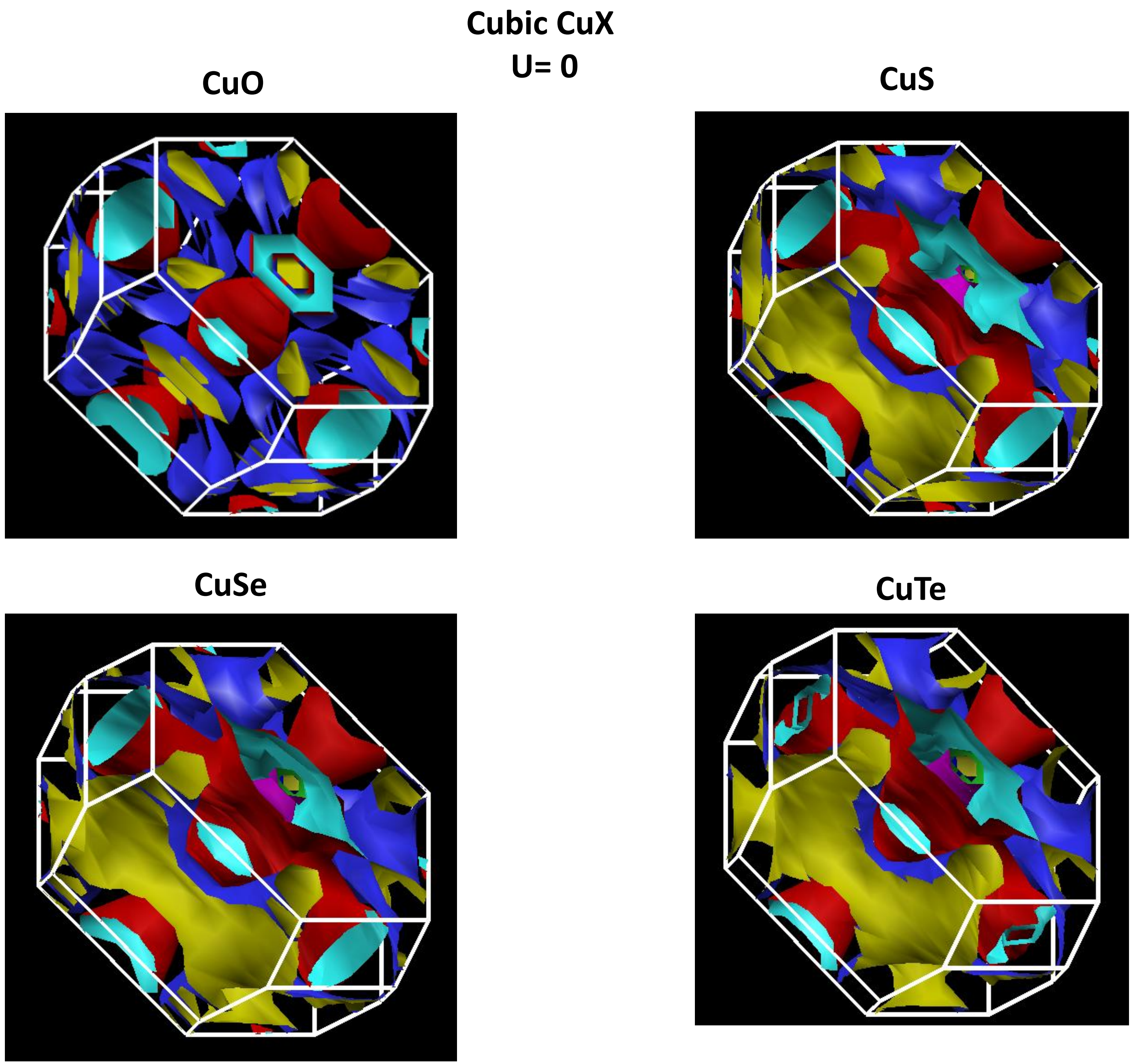


CuSe (a = b ≈ 4.75 Å; c/a ≈ 1.1)



CuTe (a = b ≈ 5.05 Å; c/a ≈ 1.1)

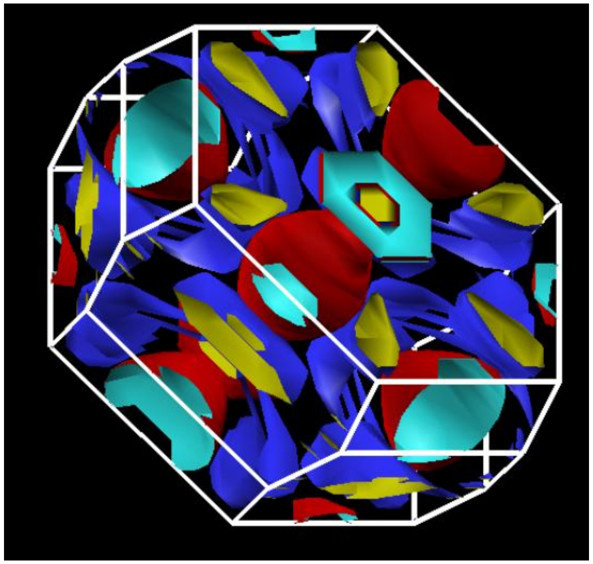




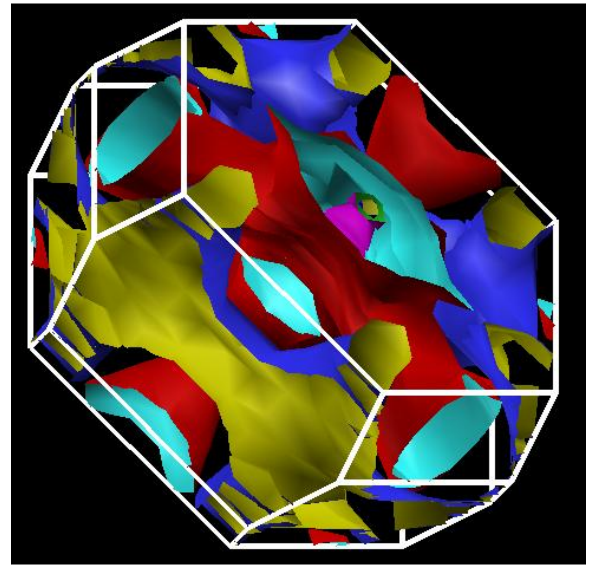
Cubic CuX
U= 0
CuO
CuS
CuSe
CuTe

Cubic CuX
U= 6

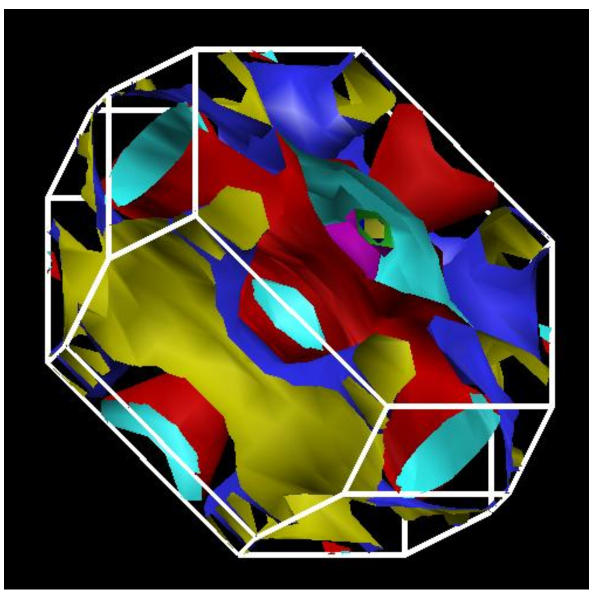
CuO



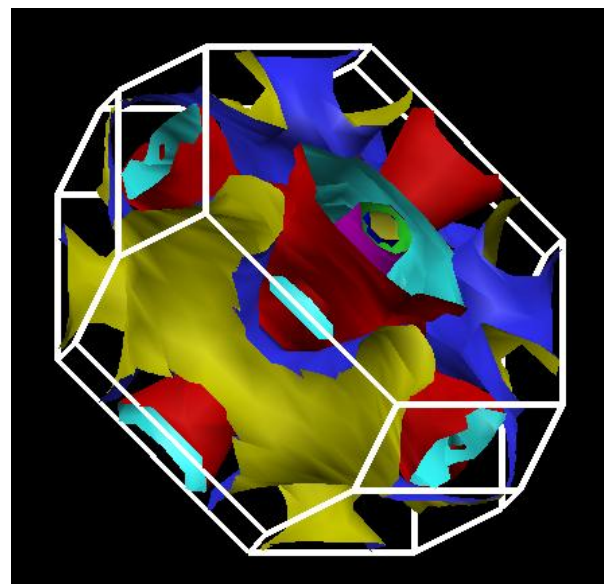
CuS

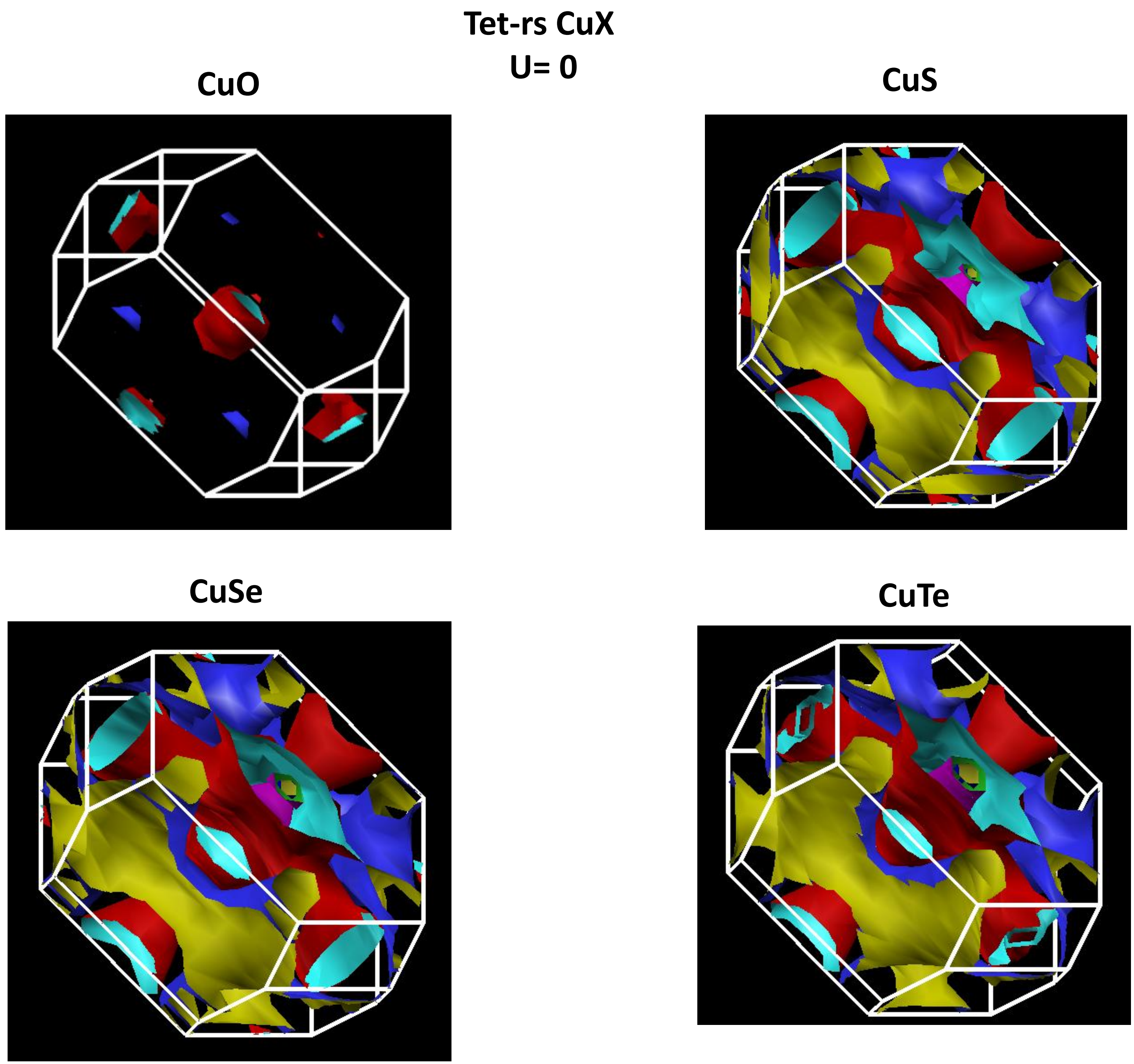


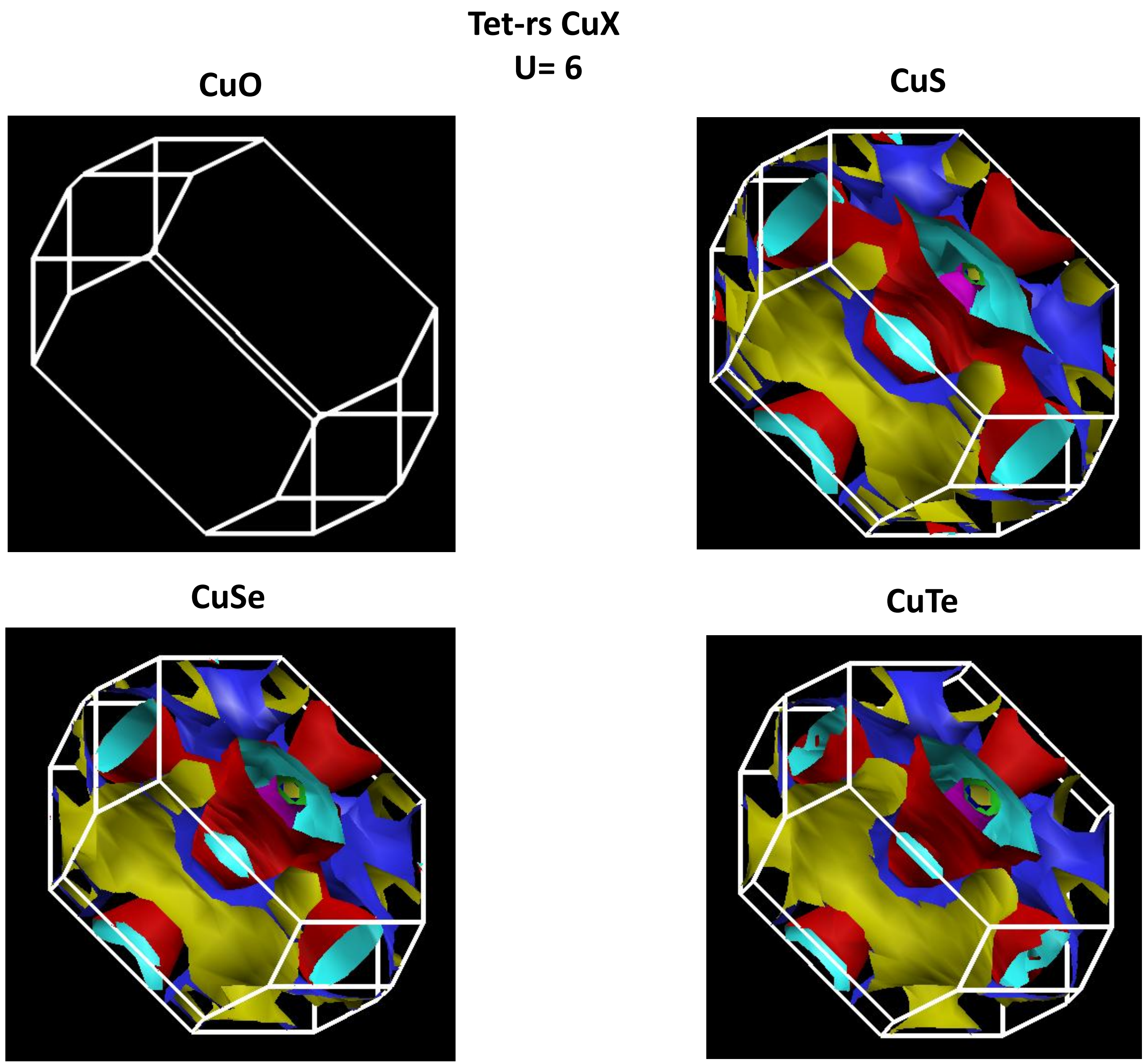
CuSe



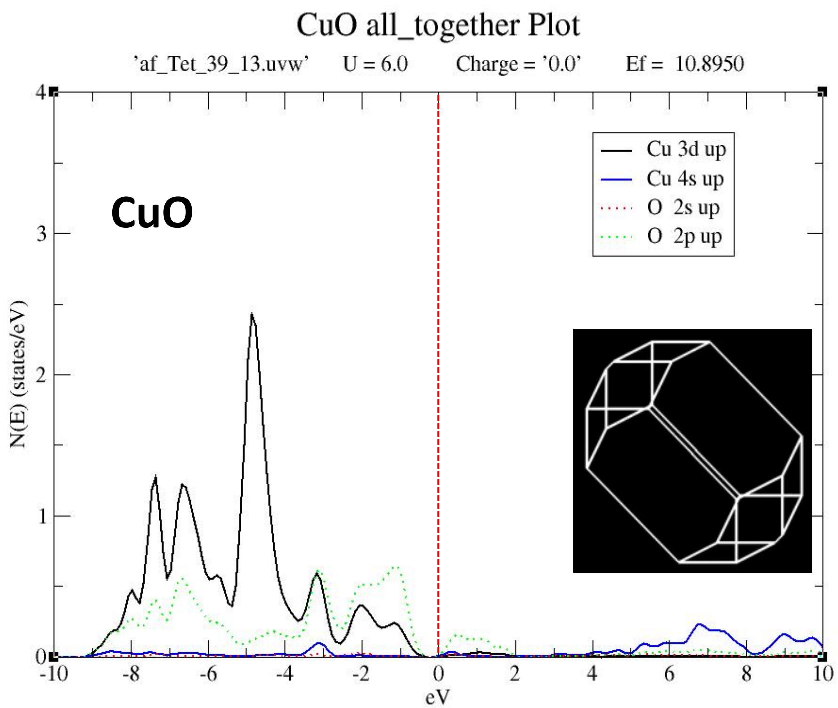
CuTe

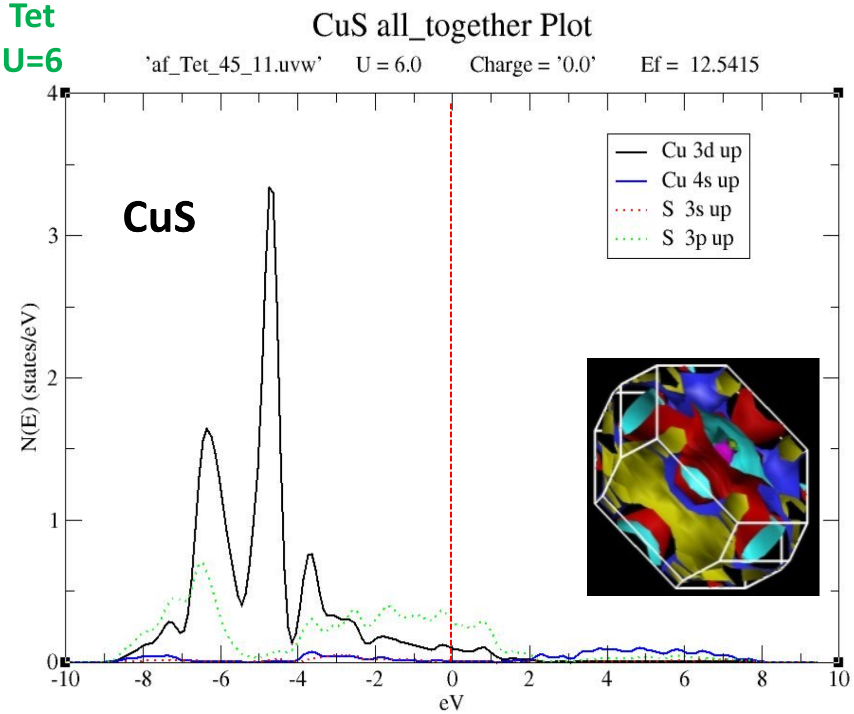


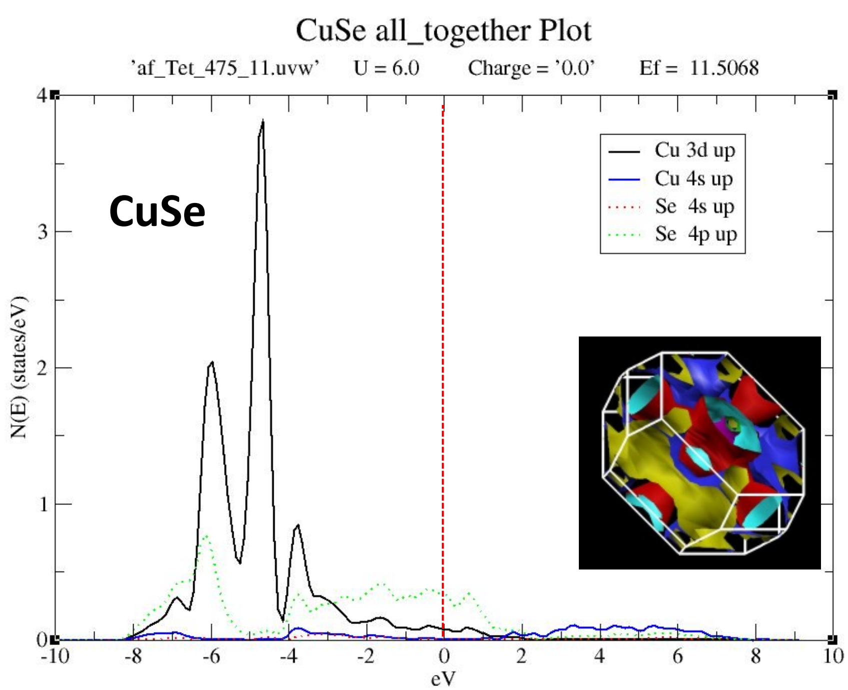

Tet-rs CuX
U= 0
CuO
CuS
CuSe
CuTe

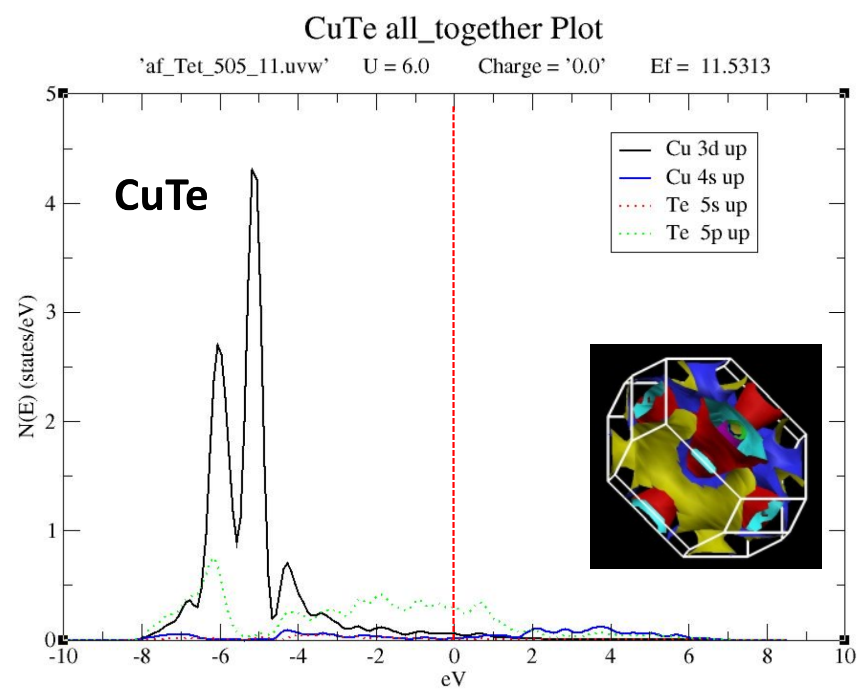

Tet-rs CuX
U= 6
CuO
CuS
CuSe
CuTe

All Tet
All U=6



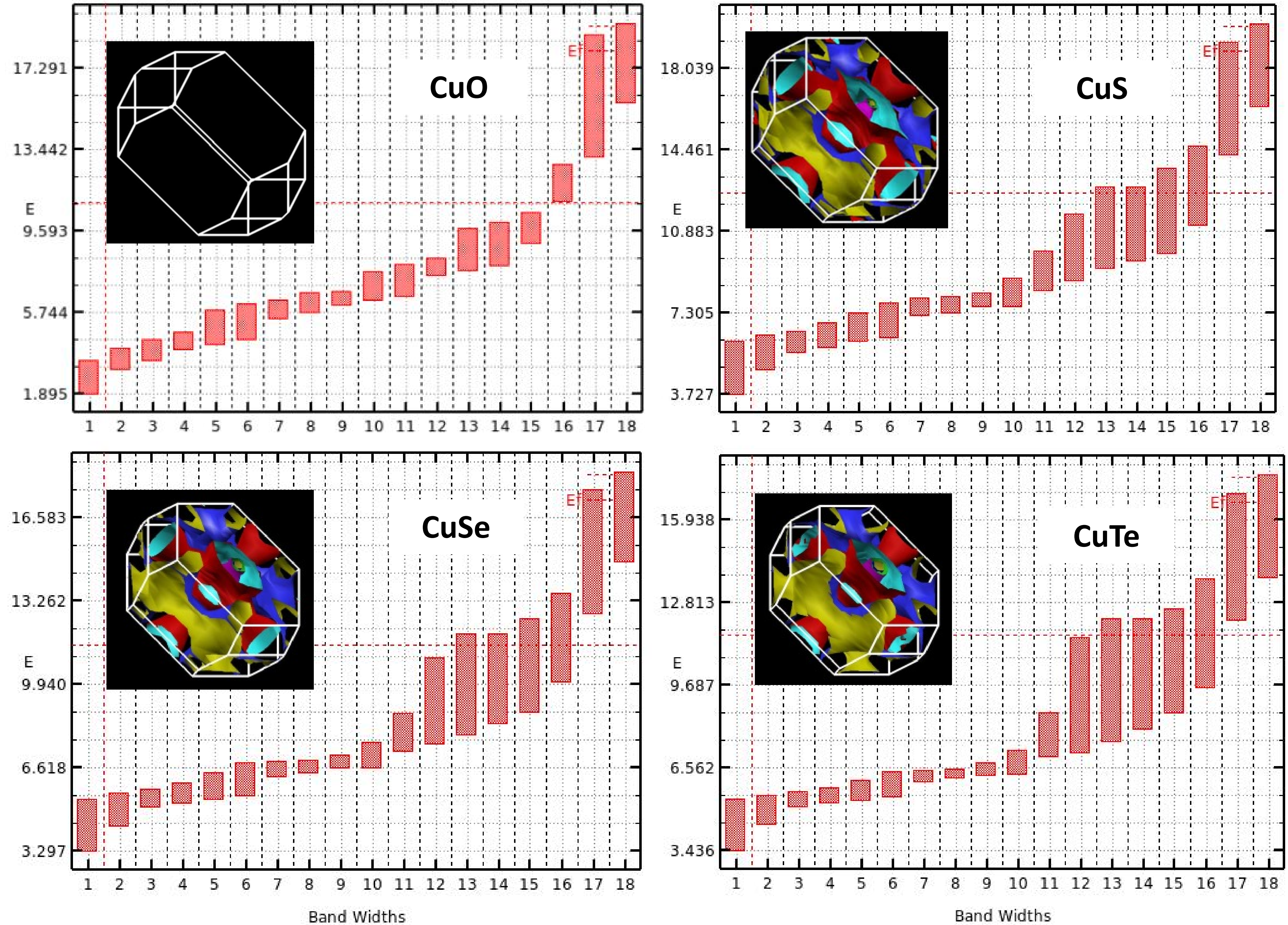






Bandwidths

All Tet. All U=6

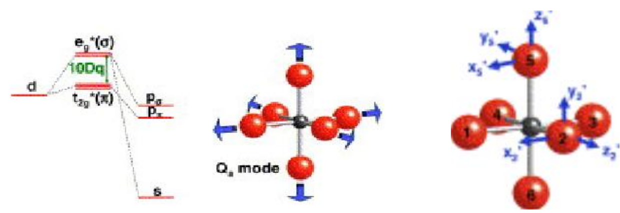


Van Vleck /Anderson/Hubbard Model of Neél Temperature

Take the definition of "Exchange Energy" from Anderson (1959):

$$J_{ij} = 2t_{ij}^2 / U$$

where t_{ij} is the transfer integral from the spin states on one TM ion, directly to a neighbor, or through an intervening anion, and U is the on-site Hubbard coulomb repulsion potential, e.g.,



Now, "plug into" Van Vleck (1938-42), within the "molecular field approximation," to get T_N:

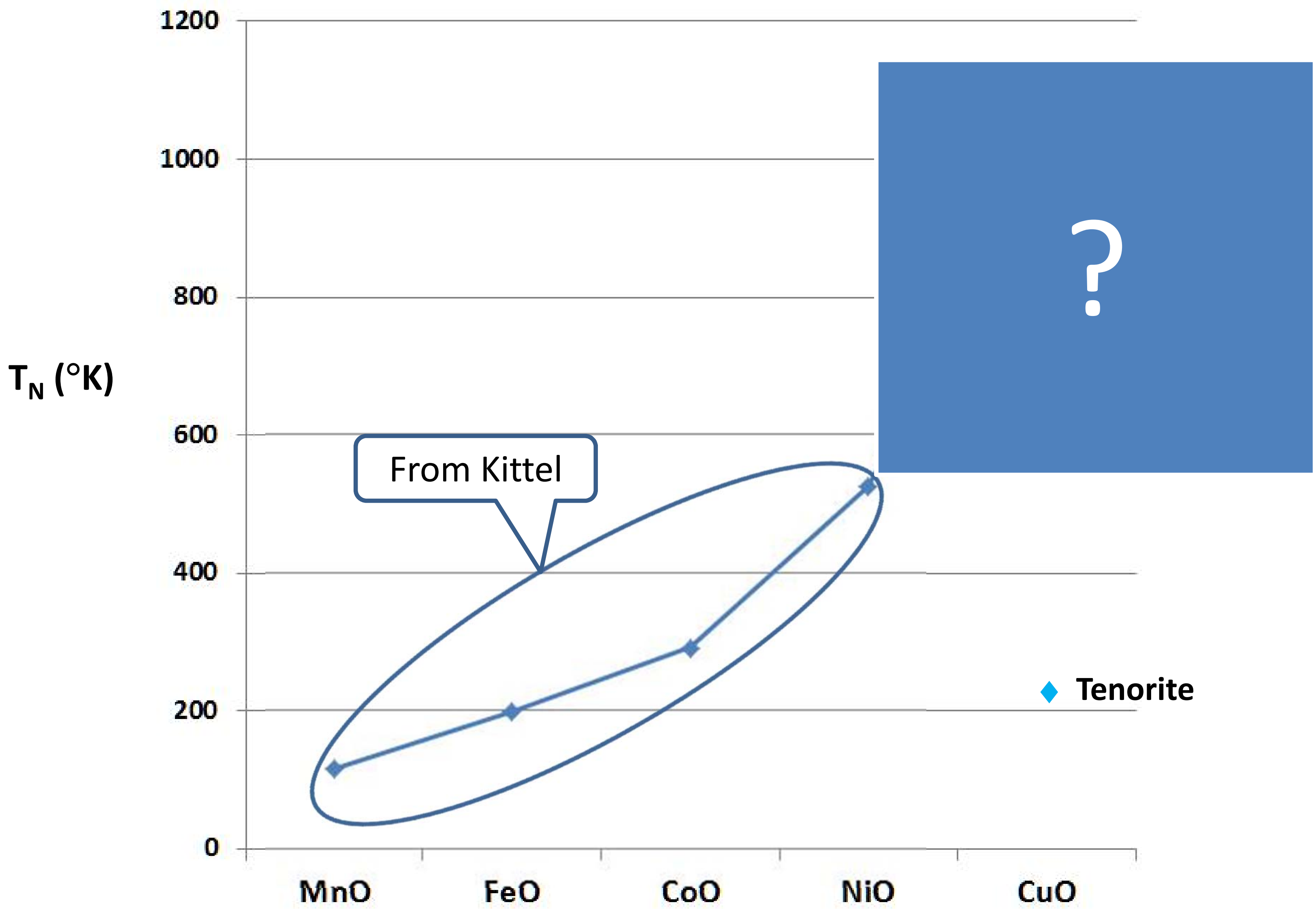
$$T_N = \frac{2S(S+1)}{3k_B} \sum_{i \neq j} J_{ij} = \frac{4S(S+1)}{3k_B U} \sum_{i \neq j} t_{i \neq j}^2$$

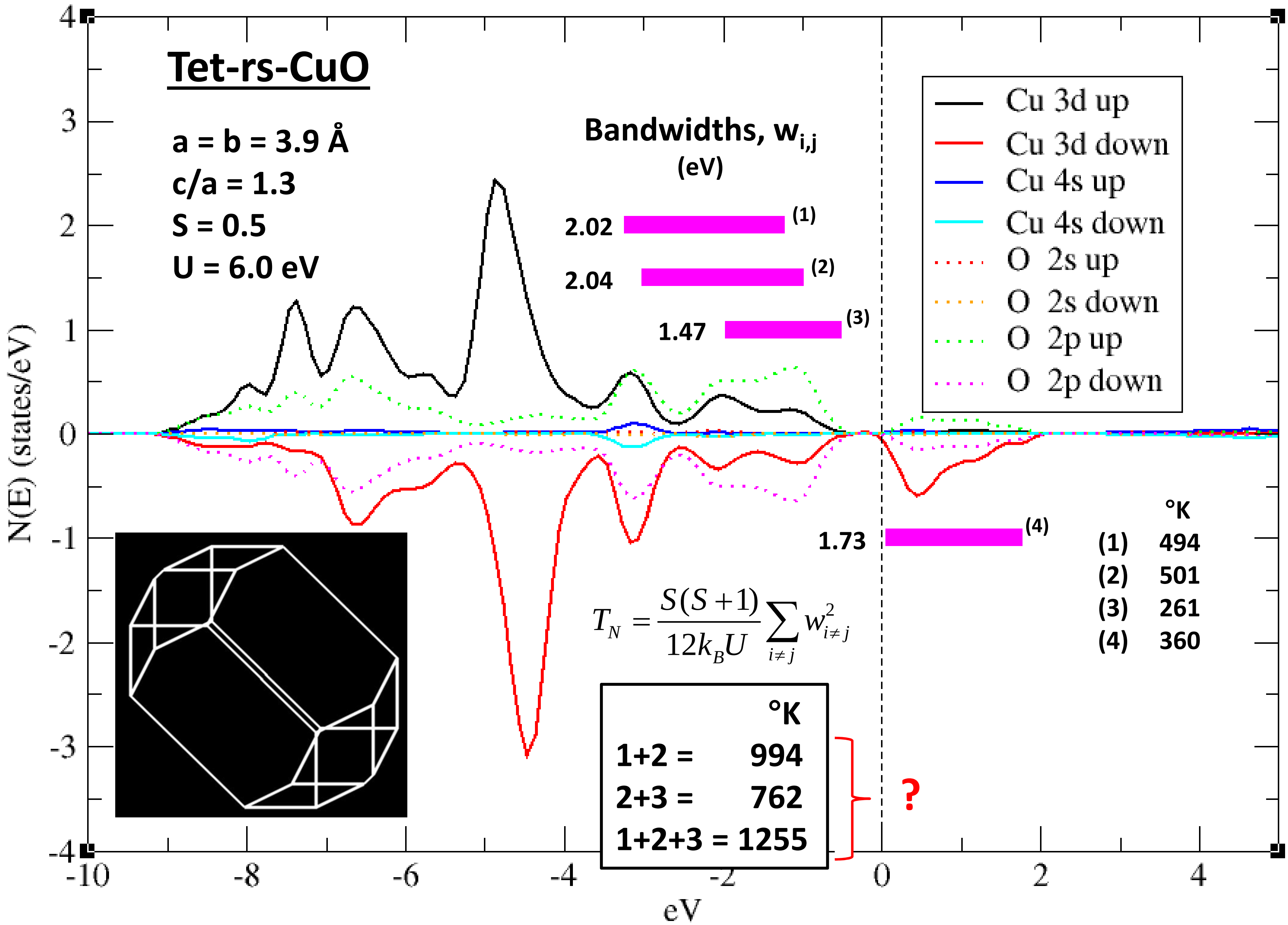
Here S is the net cationic spin and k_B the Boltzmann constant ($8.61733 \bullet 10^{-5}$ eV/°K).
The "transfer integrals" are given by,

$$t_{ij} = \left\langle \phi_j \middle| H \middle| \phi_i \right\rangle \approx \text{"} Bandwidth \text{"} / 4 = w_{i,j} / 4$$

where the ϕ's are the "spin carrying" orbitals and H a "tight-binding-like Hamiltonian."

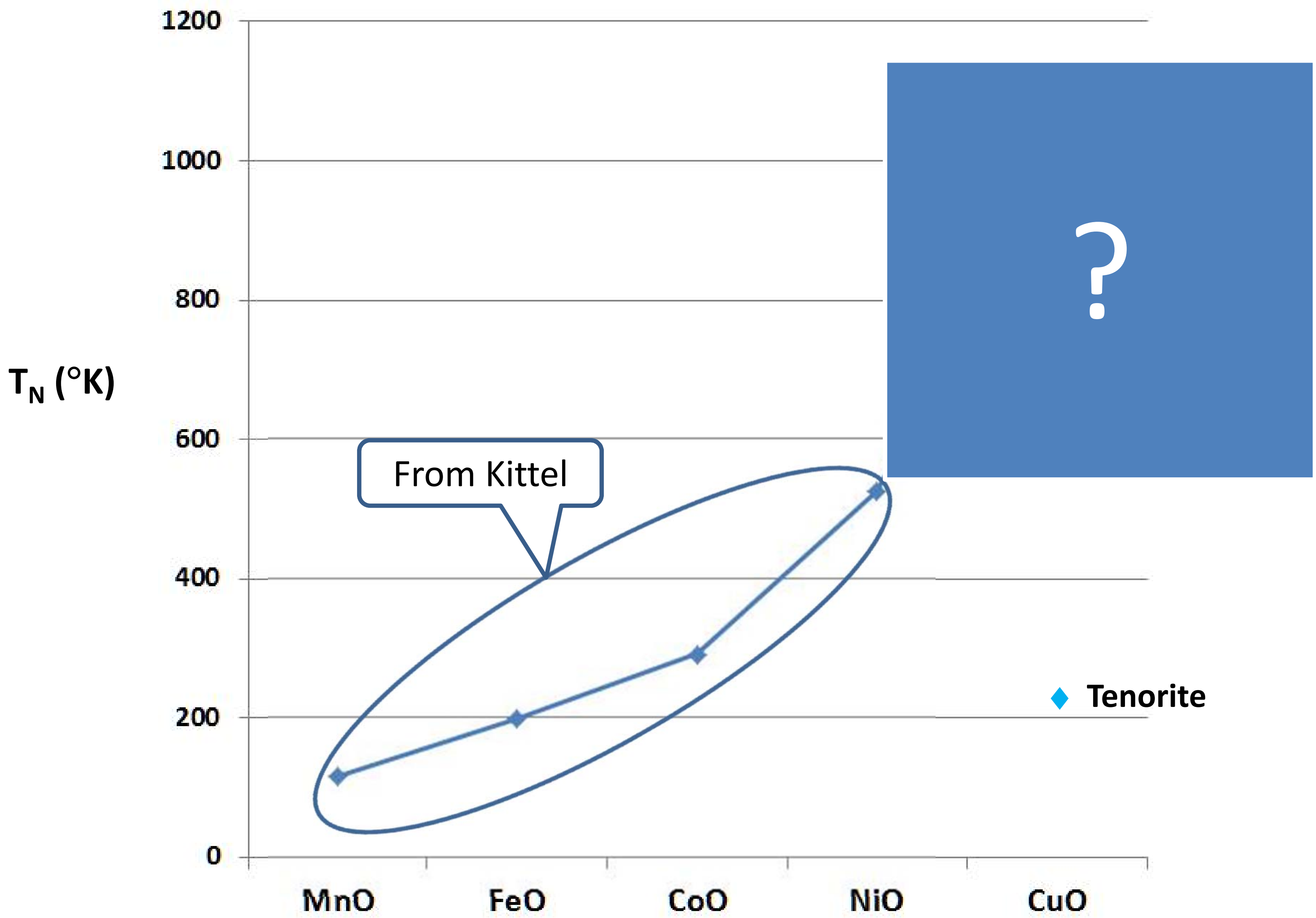
Néel Temperature vs. TMO

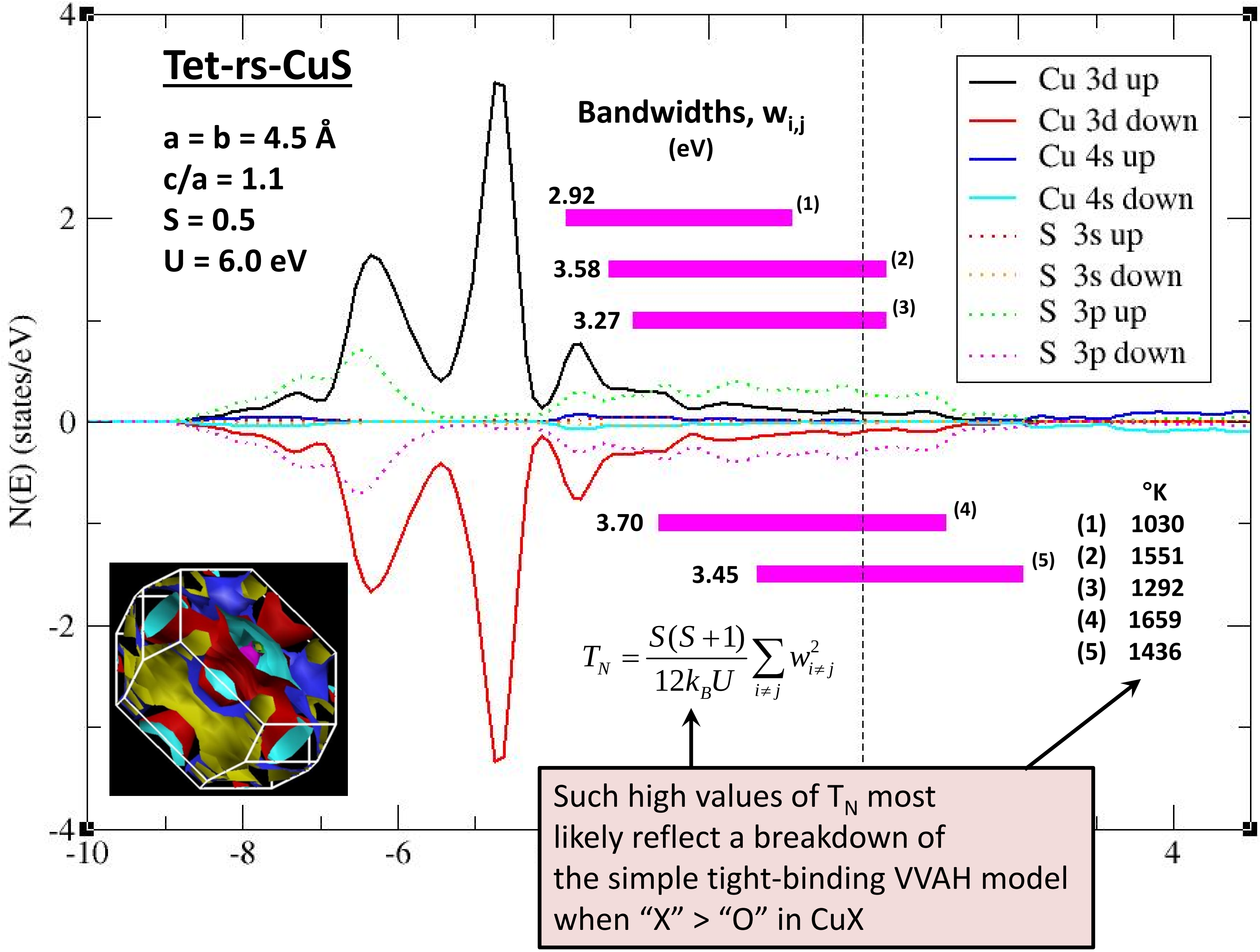




Tet-rs-CuO
a = b = 3.9 Å
c/a = 1.3
S = 0.5
U = 6.0 eV
Bandwidths, $w_{i,j}$
(eV)
2.02 (1)
2.04 (2)
1.47 (3)
1.73 (4)
Cu 3d up
Cu 3d down
Cu 4s up
Cu 4s down
O 2s up
O 2s down
O 2p up
O 2p down
°K
(1) 494
(2) 501
(3) 261
(4) 360
$T_N = \frac{S(S+1)}{12k_B U}\sum_{i\neq j} w_{i\neq j}^2$
°K
1+2 = 994
2+3 = 762
1+2+3 = 1255
?
N(E) (states/eV)
eV

Néel Temperature vs. TMO





Tet-rs-CuS
a = b = 4.5 Å
c/a = 1.1
S = 0.5
U = 6.0 eV
Bandwidths, $w_{i,j}$
(eV)
2.92 (1)
3.58 (2)
3.27 (3)
3.70 (4)
3.45 (5)
Cu 3d up
Cu 3d down
Cu 4s up
Cu 4s down
S 3s up
S 3s down
S 3p up
S 3p down
°K
(1) 1030
(2) 1551
(3) 1292
(4) 1659
(5) 1436
$T_N = \frac{S(S+1)}{12 k_B U} \sum_{i \neq j} w_{i \neq j}^2$
Such high values of T_N most likely reflect a breakdown of the simple tight-binding VVAH model when “X” > “O” in CuX
N(E) (states/eV)
4
2
0
-2
-4
-10
-8
-6
4

Superconductivity(?) Phonons(?)

Eliashberg-McMillan

$$H_{el-ph} = \sum_{\mathbf{k},\mathbf{q},\nu} g_{\mathbf{k+q},\mathbf{k}}^{\mathbf{q}_\nu,mn} c_{\mathbf{k+q}}^{\dagger m} c_{\mathbf{k}}^{n} (b_{-\mathbf{q},\nu}^{\dagger} + b_{\mathbf{q},\nu})$$

$$\lambda_{\mathbf{q},\nu} = \frac{2}{N(\varepsilon_F)\omega_{\mathbf{q},\nu}} \sum_{mn} \sum_{\mathbf{k}} \left| g_{\mathbf{k+q},\mathbf{k}}^{\mathbf{q}_\nu,mn} \right|^2 \delta(\varepsilon_{\mathbf{k+q},m} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F)$$

$$\alpha^2 F(\omega) = \frac{1}{N(\varepsilon_F)} \sum_{mn} \sum_{\mathbf{q},\nu} \delta(\omega - \omega_{\mathbf{q},\nu}) \sum_{\mathbf{k}} \left| g_{\mathbf{k+q},\mathbf{k}}^{\mathbf{q}_\nu,mn} \right|^2 \delta(\varepsilon_{\mathbf{k+q},m} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k},n} - \varepsilon_F)$$

$$\lambda = 2\int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega = \sum_{\mathbf{q},\nu} \lambda_{\mathbf{q},\nu}$$

Need to compute $g_{\mathbf{k+q},\mathbf{k}}^{\mathbf{q}_\nu,mn}$!

e-p Interaction in the DFT/LDA Formalism

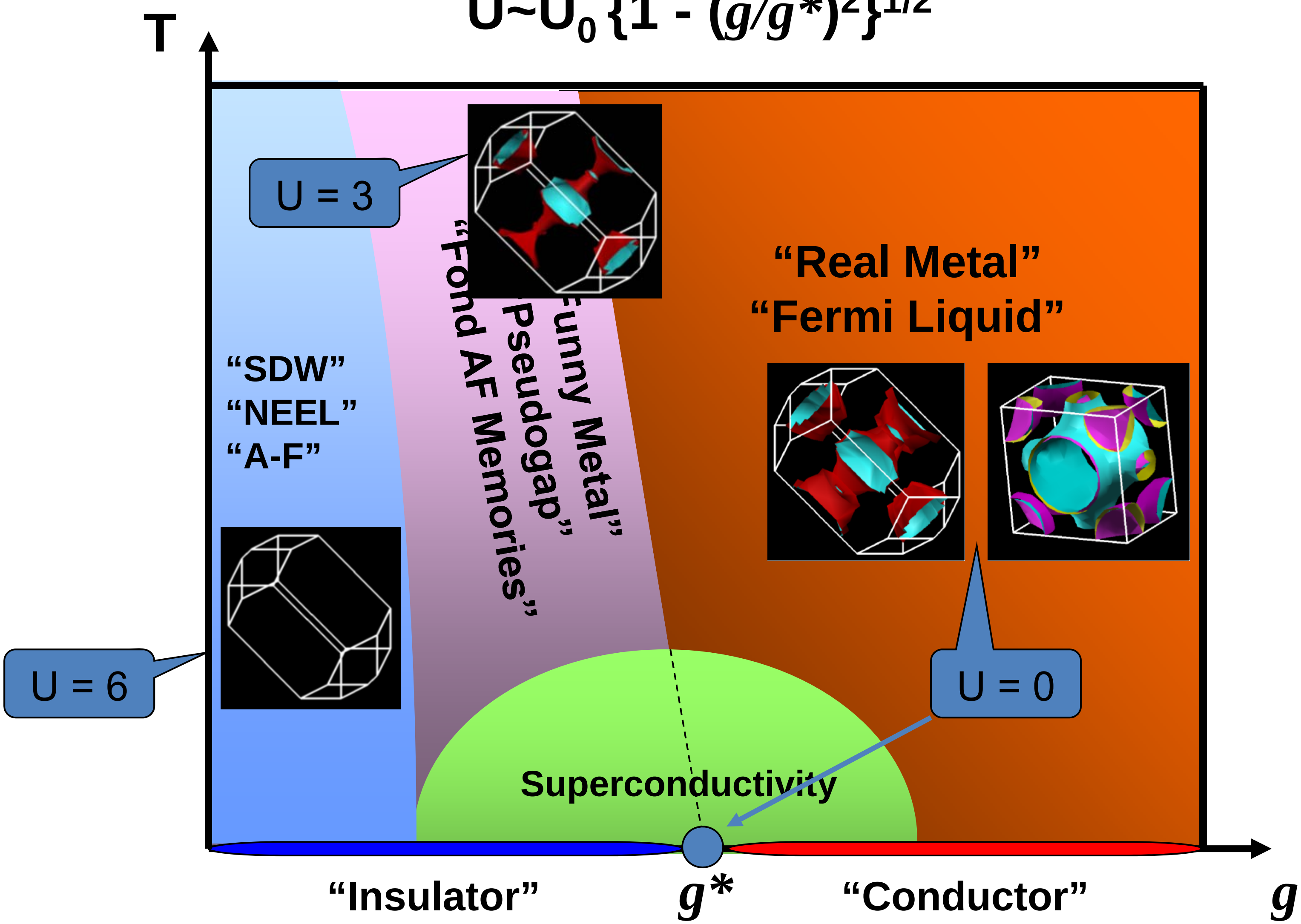
$$g_{\mathbf{k}+\mathbf{q},\mathbf{k}}^{\mathbf{q}_{\nu},mn} = \sqrt{\hbar / 2\omega_{\mathbf{q},\nu}} \left\langle \psi_{\mathbf{k}+\mathbf{q},m} \middle| \Delta V_{KS}^{\mathbf{q},\nu} \middle| \psi_{\mathbf{k},n} \right\rangle$$

$$\Delta V_{KS}^{\mathbf{q},\nu} = \sum_{\mathbf{R}} \sum_{s} \frac{\partial V_{KS}}{\partial \vec{u}_{s,\mathbf{R}}} \cdot \vec{u}_{s}^{\mathbf{q},\nu} \frac{e^{i\mathbf{q}\cdot\mathbf{R}}}{\sqrt{N}}$$

$$T_C = \frac{\Theta_D}{1.45} \exp\left(- \frac{1.04\left(1+\lambda\right)}{\lambda - \mu^{*}\left(1+0.62\lambda\right)} \right)$$

The Colossal Quantum Conundrum

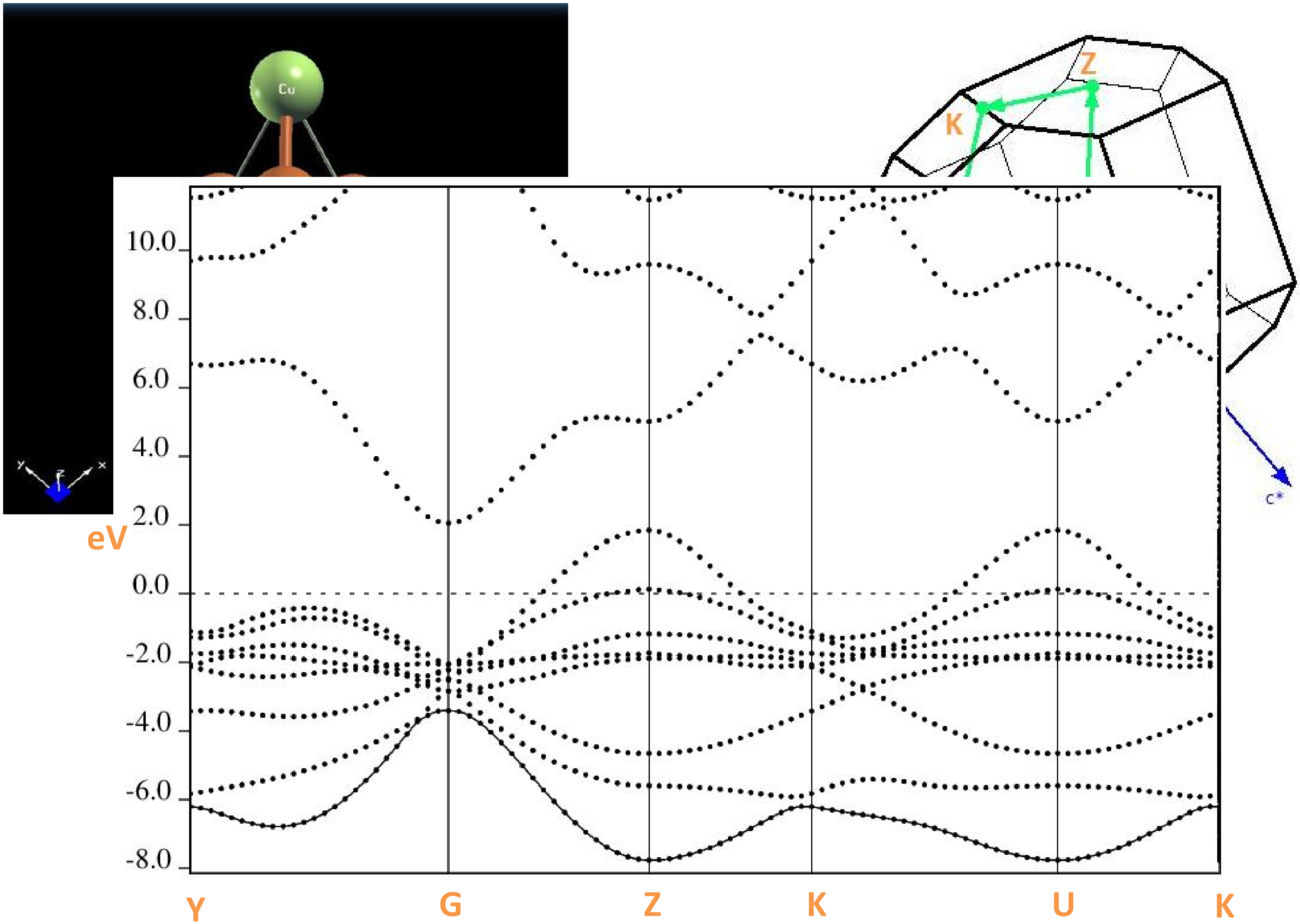
$$U \sim U_0 \{1 - (g/g^*)^2\}^{1/2}$$



Somewhere in here there has to be “BCS-like” pairing!

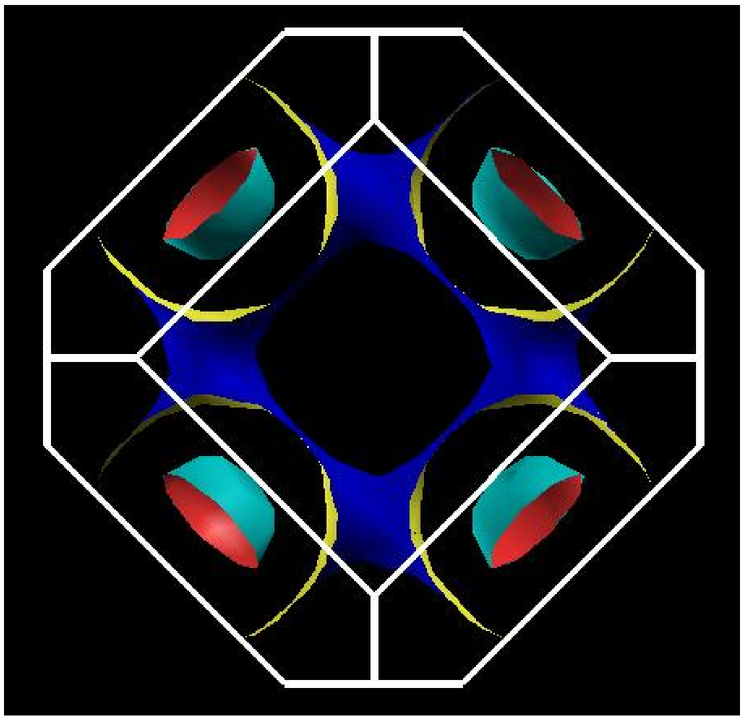
Perhaps phonon-mediated?

Well, how about the "U = 0, Fermi Liquid" limit for doped proxy tet-CuO?



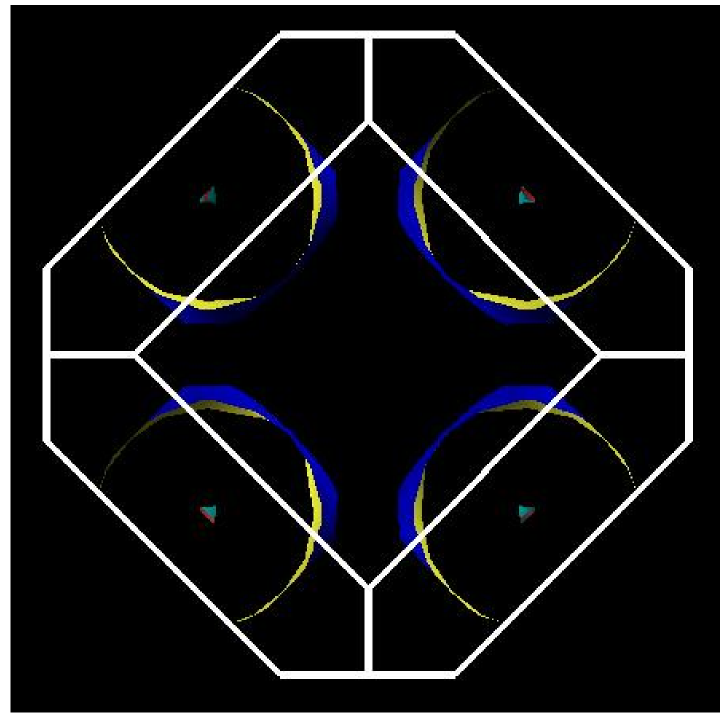
So let's do it and "compute" what happens!

q = 0.15 |e|/CuO (holes)



≈ 43 °K

q = -0.15 |e|/CuO (electrons)



≈ 25 °K

Apply DFT to obtain $g^{\mathbf{q}_{\nu,mn}}_{\mathbf{k}+\mathbf{q},\mathbf{k}}$ between electrons and phonons, followed by application of the Eliashberg-McMillan-Allen-Dynes formalism to find Tc:

Can We Really Make Any of This Stuff?

Forced-epitaxial thin film growth is obvious choice (as it was with tet-CuO. Substrate selection likely limited, but here are possible choices:

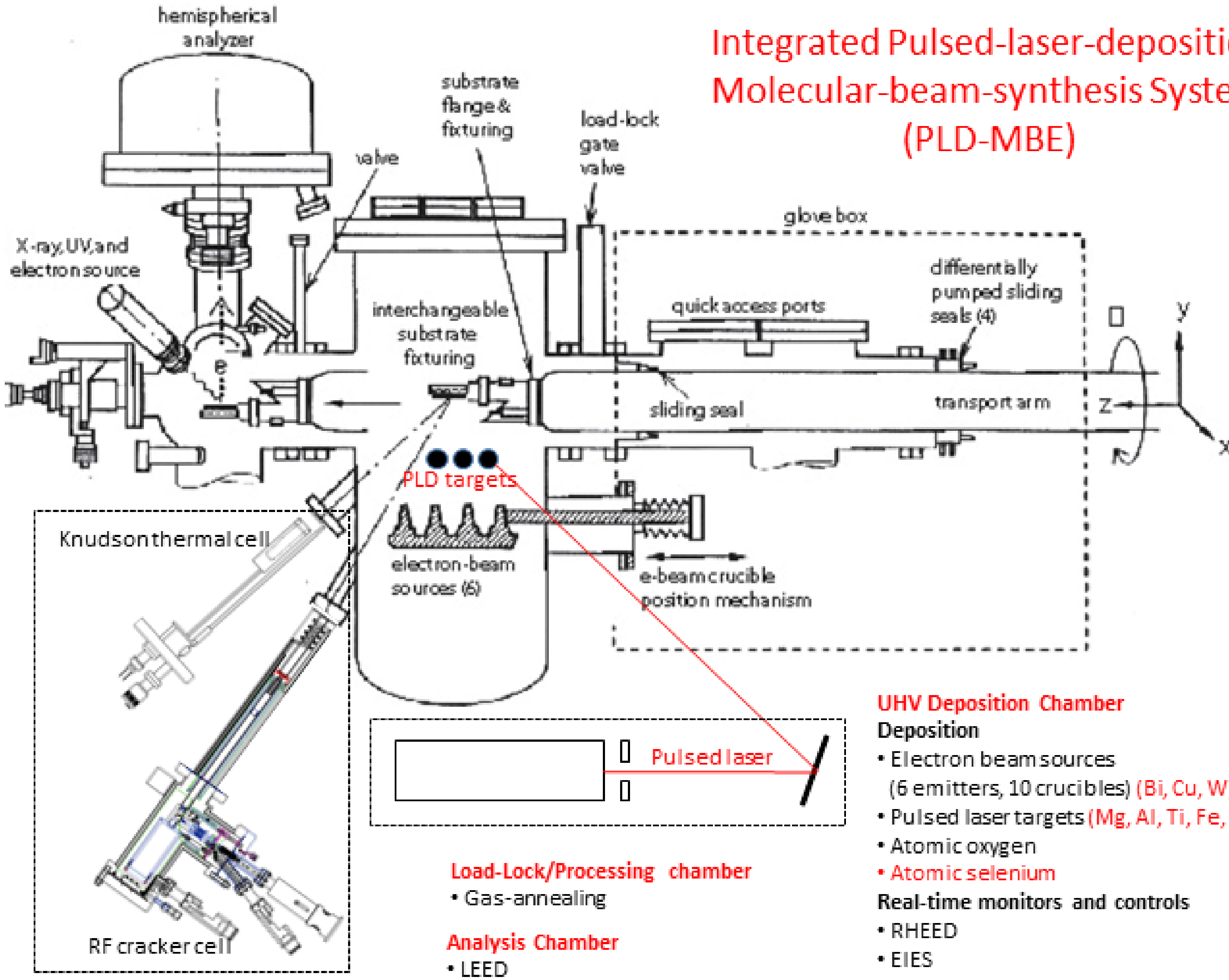
1. CuS (4.7 Å) — Rocksalt ZnO (4.580 Å, ~3% compression)
   Rutile TiO_2 (4.591 Å, ~2.5% compression)
2. CuSe (5.0 Å) — Hex Al_2O_3 (4.748 Å, ~5% compression)
3. CuTe (5 .3 Å) — Cubic ZrO_2 (5.147 Å, ~5.3% compression)
   YSZ (5.13 – 5.23 Å, ~3.5% compression max)
   CaF (5.46 Å, ~3% expansion)

Methodologies

a) MBE - PLD:
   i. Use appropriate sintered sample source.
   ii. Empirically determine optimum substrate temperature and argon pressure.
   iii. Characterize growth and structure via in-situ “high pressure compatible” RHEED, XPS, UPS, LEED.
b) External characterization, depending on stability in air:
   i. 4-probe transport.
   ii. UV-Vis optical transmission and reflectivity.

“An Ideal Lab”

Integrated Pulsed-laser-deposition Molecular-beam-synthesis System (PLD-MBE)



Load-Lock/Processing chamber
- Gas-annealing

Analysis Chamber
- LEED
- XPS
- UPS

UHV Deposition Chamber

Deposition
- Electron beam sources (6 emitters, 10 crucibles) (Bi, Cu, W)
- Pulsed laser targets (Mg, Al, Ti, Fe, Ni)
- Atomic oxygen
- Atomic selenium

Real-time monitors and controls
- RHEED
- EIES
- QCM
- Atomic absorption rate control

The Bottom Line(s)

- For X = S, Se and Te, neither a finite U or a “5% basal” tetragonal distortion has much effect on their respective CuX Fermiologies, and likely transport/magnetic properties dependent thereon.
- However, the respective Fermi surfaces ...may...may... contain nesting topologies promoting itinerant antiferromagnetism a la Cr, but, unlike Cr, here for X = S, Se, Te, the DOS at Ef is dominated by p-like chalcogenide overlap.
- Future homework for proxy structure modelling, suggested by preliminary results on “doped” tet-CuO: Let’s look for electron-phonon mediated superconductivity!
- But ...most importantly... experiment *always* rules. Our fundamental computational finding is that equilibrium rocksalt CuS, CuSe and CuTe structures can in principle exist ...so let’s try to make and dope them and henceforth measure their properties!

Finally, there is something quite special about the Cu-O bond in square-planar symmetry!

...but we knew that already... in 1986 B & M told us so!